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Uranium Battery Update for KRCEE

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Paducah Extension Campus

Paducah Gaseous Diffusion

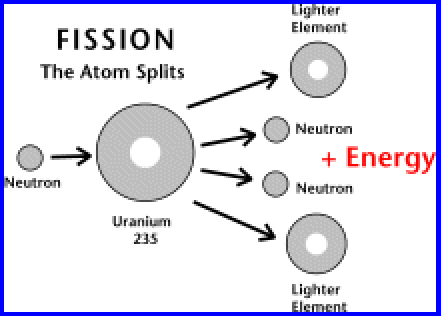
- 5 Billion Pounds of Depleted Uranium in Paducah
- $200M Conversion Plant Under Construction
  - Convert UF_6 to U_3O_8
- Low Radiation Levels for depleted uranium 0.1% U_{235} compared to 0.7% U_{235} for natural uranium
  - Great source for U_3O_8

Uranium Properties on Paper

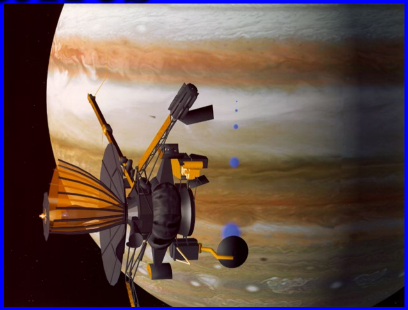
- **Uranium Standard Reduction Potential Voltage of 4.7 Volts per Cell from U to $UO_2(OH)_2$ (in alkaline environment)**
- **Lithium is 3V per cell**
- **Lead is 2V per cell**
- **U can supply 6 electrons instead of 2**
  - **In reality it is less than 3 electrons**
- **Uranium is a Highly reactive materials**

Potential for compact battery
With a high power density

$$UO_2(OH)_2 \xleftrightarrow{-0.3V} UO_2 \xleftrightarrow{-2.6V} U(OH)_3 \xleftrightarrow{-2.10V} U$$



Collaborators and Consultants



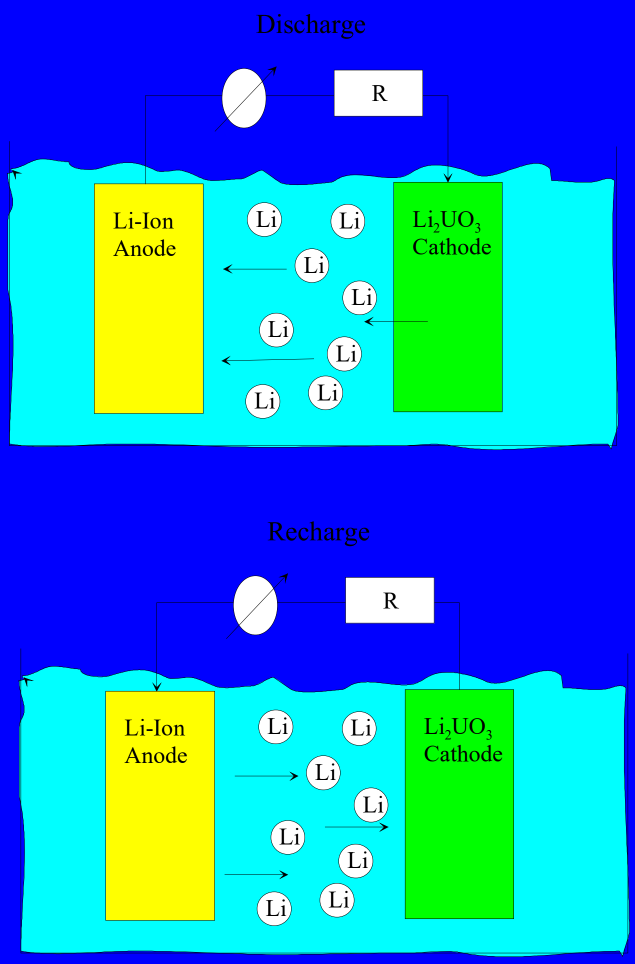
- Walter Tracinski
  - Applied Power International (Idaho) Lithium Battery Expert
  - B.S. Chemistry RPI
  - Consultant to US Navy, US Air Force, and The Boeing Company. Contracts for batteries on F-18s and F-16s.
  - Tested the Galileo spacecraft batteries (500,000 cycles to pass the recharge/discharge)
- Dr. Stephen Lipka
  - Center for Applied Energy Research UK -Electrochemist/Material Scientist,
- Dr. Richard Howard
  - Inorganic Chemist--Battery Materials Consultant (25 years experience in Industry) Developed Cathode materials for Kerr-McGee

Technical Project Goals

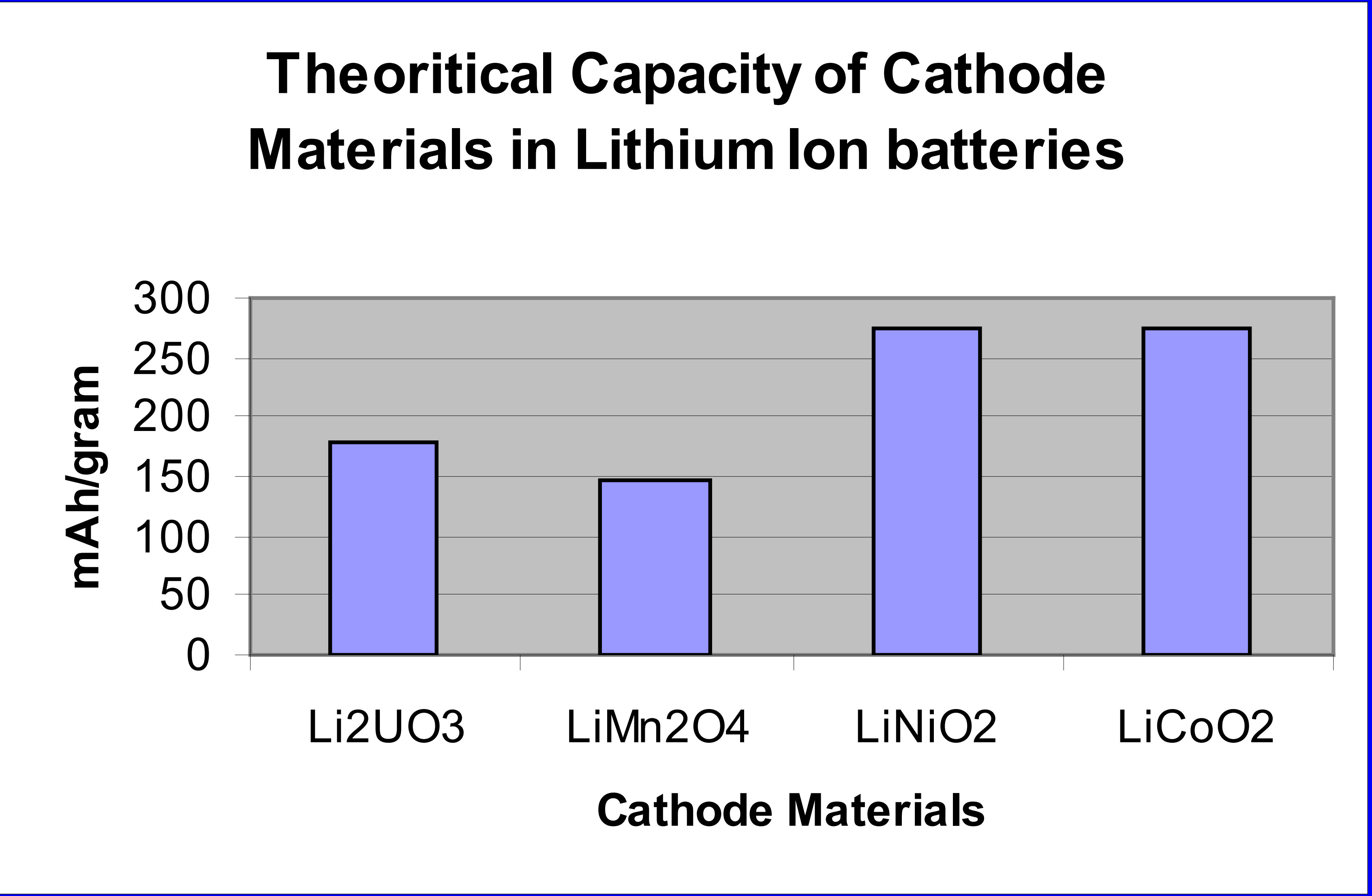
- Mirror the development of manganese dioxide and lithiated manganese oxides as battery materials
  - Characterize uranium dioxide and lithiated uranium oxide’s electrochemical properties in various commercial organic solvents/lithium salts
  - Build cells and test using common electrochemical methods
    - cyclic voltammetry
    - impedance spectroscopy
  - Use this information to construct a battery
    - Lithiated Uranium Oxides will allow for lithium intercalation
    - Based on theory Li_2UO_3 is the best candidate

Current Work

- Optimize Lithiated Material as Cathode
  - Intercalation Behavior
- UO_2 and U_3O_8 as Capacitor
- Lithiated uranium oxides as capacitors
- Uranium doped lithiated metal oxides to enhance performance



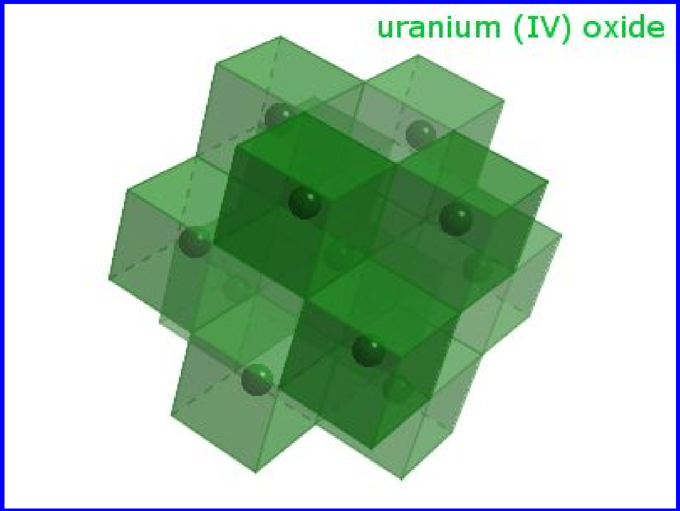
ReCharge and Discharge of Lithium-Ion Anode and Lithiated Uranium dioxide Cathode Battery



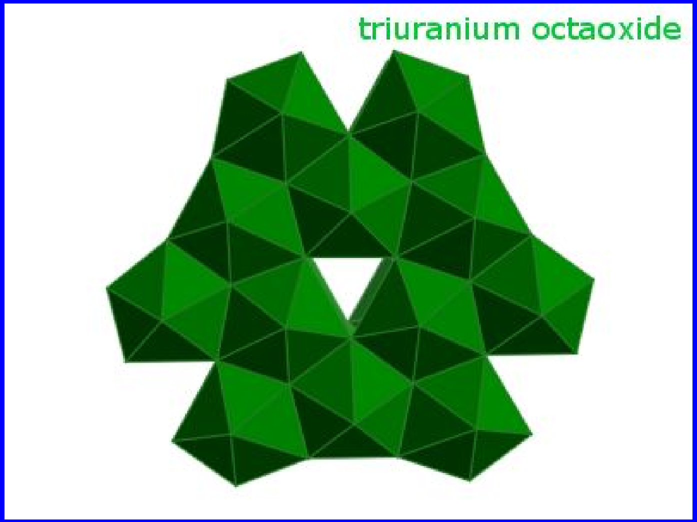
Battery limited by the rate at which the cathode can receive the electrons
From the anode.

Analysis of Products

- Structure and Composition
  - X-Ray Diffraction
  - X-Ray Fluorescence



- Electrochemical Behavior
  - Cyclic Voltammetry
  - Impedance Spectroscopy



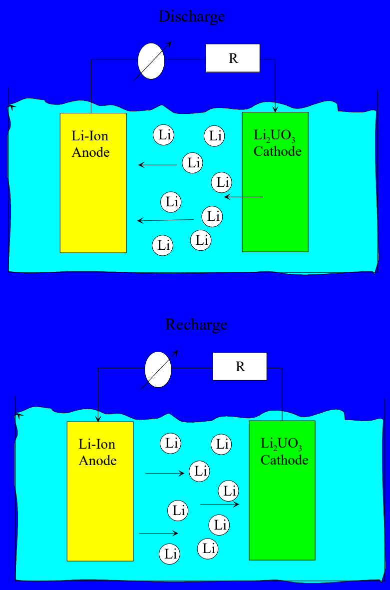
Cyclic Voltammetry Experiments

- Technique used for determine formal potential for a half reaction.
- Looking for redox potentials of electroactive species
- Linear potential sweep of working electrode with measurement of current.
- Plot of current vs. potential is cyclic voltammogram.

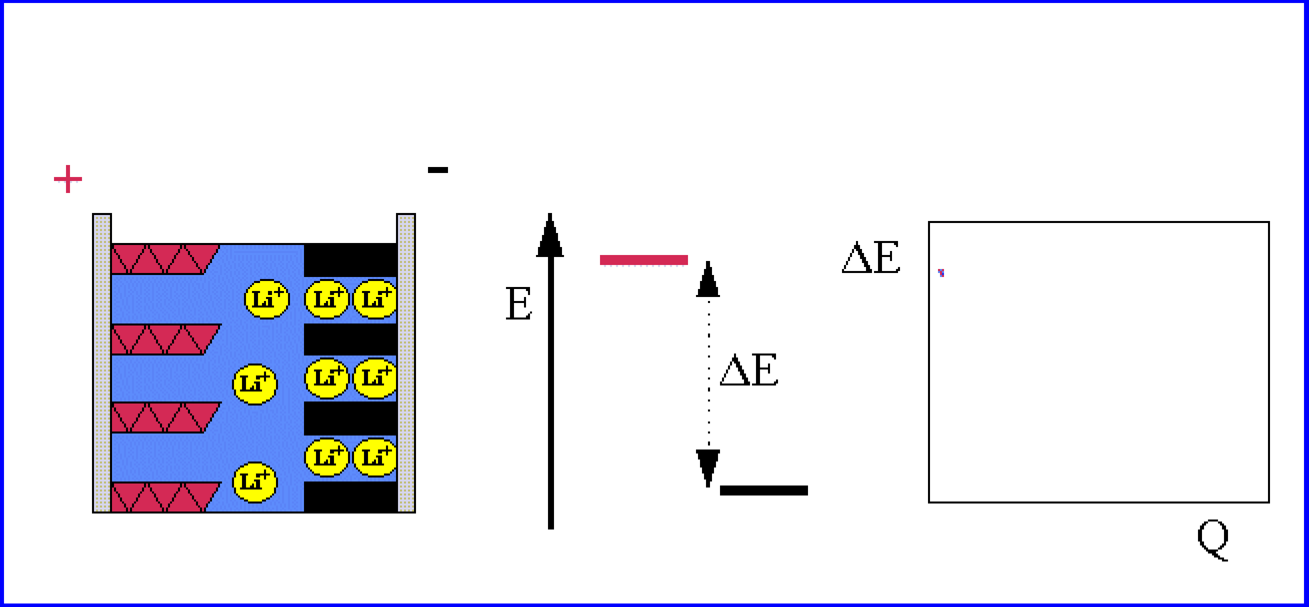
Lithiated Compounds

- Make Li_2UO_3 with a $^+4$ Valence
  – Based on Phase Diagrams and the Literature
- Tube Furnace is required to create a reducing atmosphere
  – 5% Hydrogen 95% Argon in a tube furnace
  – U_3O_8 + Li(OH)*H_2O $\longrightarrow$ Li_2UO_3

Animation of Lithium-Ion Cell



ReCharge and Discharge of Lithium-Ion Anode and Lithiated Uranium dioxide Cathode Battery



Cathodes must have crystal structure to allow re-intercalation

Load leveling battery

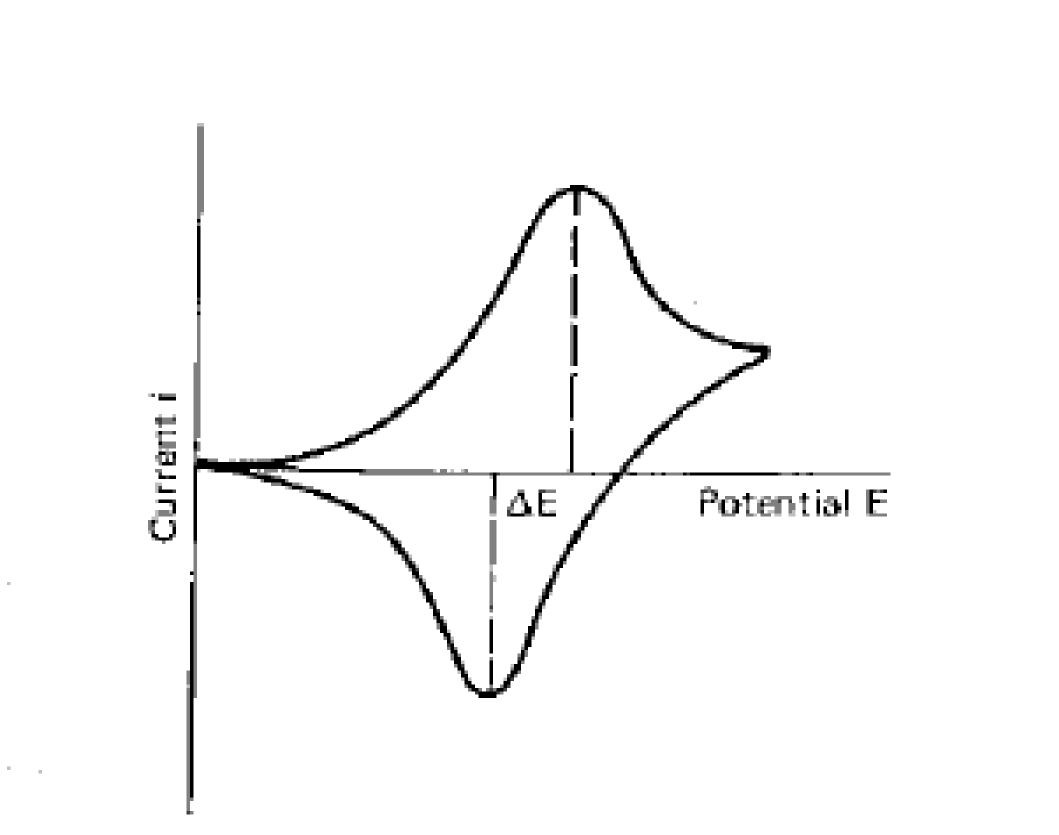
- $10 Billion a year business
- Potential Markets
  - Energy Storage, Load Leveling, and Thermal batteries, Military Applications (Radar stations etc.)
- Secondary Battery
  - Rechargeable
  - High power density
  - Good performance at desired temperature
- Currently lead acid is used as load leveling (Pb/PbO_2 in H_2SO_4)
- Japanese are working on lithium-ion load leveling batteries
  - Combining large number of cells

http://www.sei.co.jp/sn/2001/09/6b.html

Lithiated Uranium Oxide Material

- Load Leveling Battery
  - 2,000 Amp-hours with 24.5 lbs
  - 15,000 Amp-hours with 183.75 lbs
- Southern California Edison has a load leveling battery with 8256 cells with each of 3250 Amp-hours
  - 164 tons of uranium materials
- 10 Billion pounds could produce 50 million batteries at 200 pounds a piece

Textbook CV of reversible, diffusion controlled process



Literature CVs of Lithiated Metal Oxides – Rao, et. al.

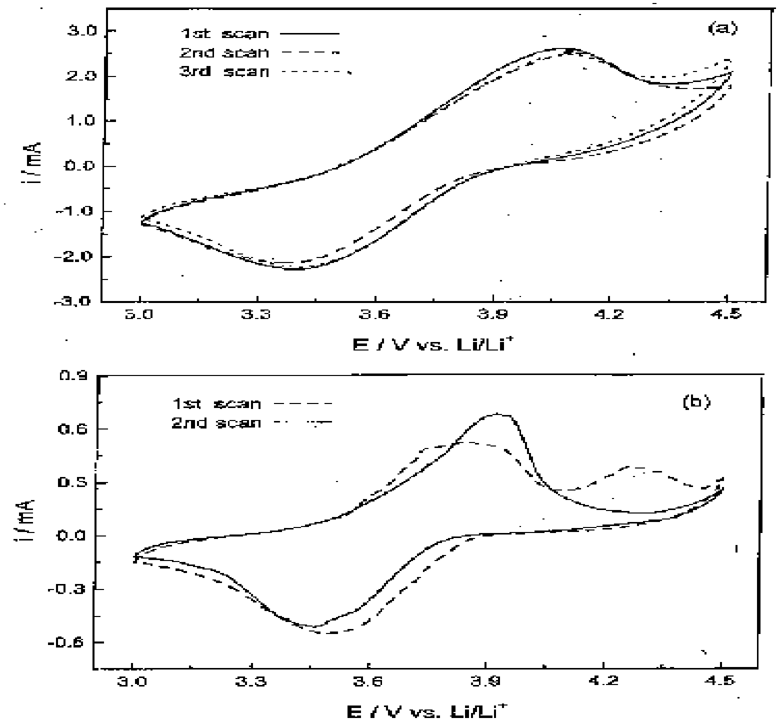


Fig. 3 Cyclic voltammograms of the $Li_{0.88}Ni_{1.12}O_2$ electrode at scan rates of **a** 0.1 mV s^{-1} and **b** 0.01 mV s^{-1}, with 1 M $LiClO_4$ in PC as the electrolyte

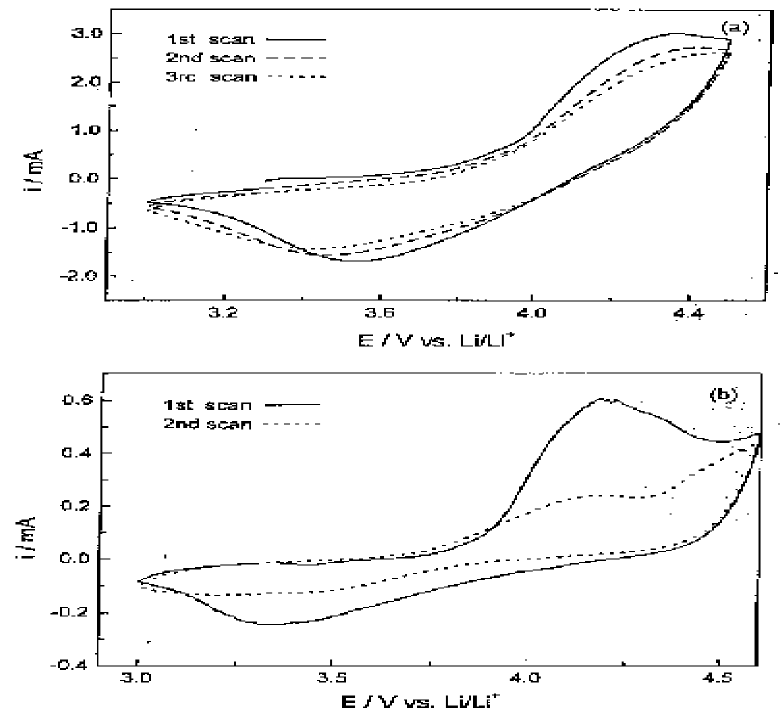
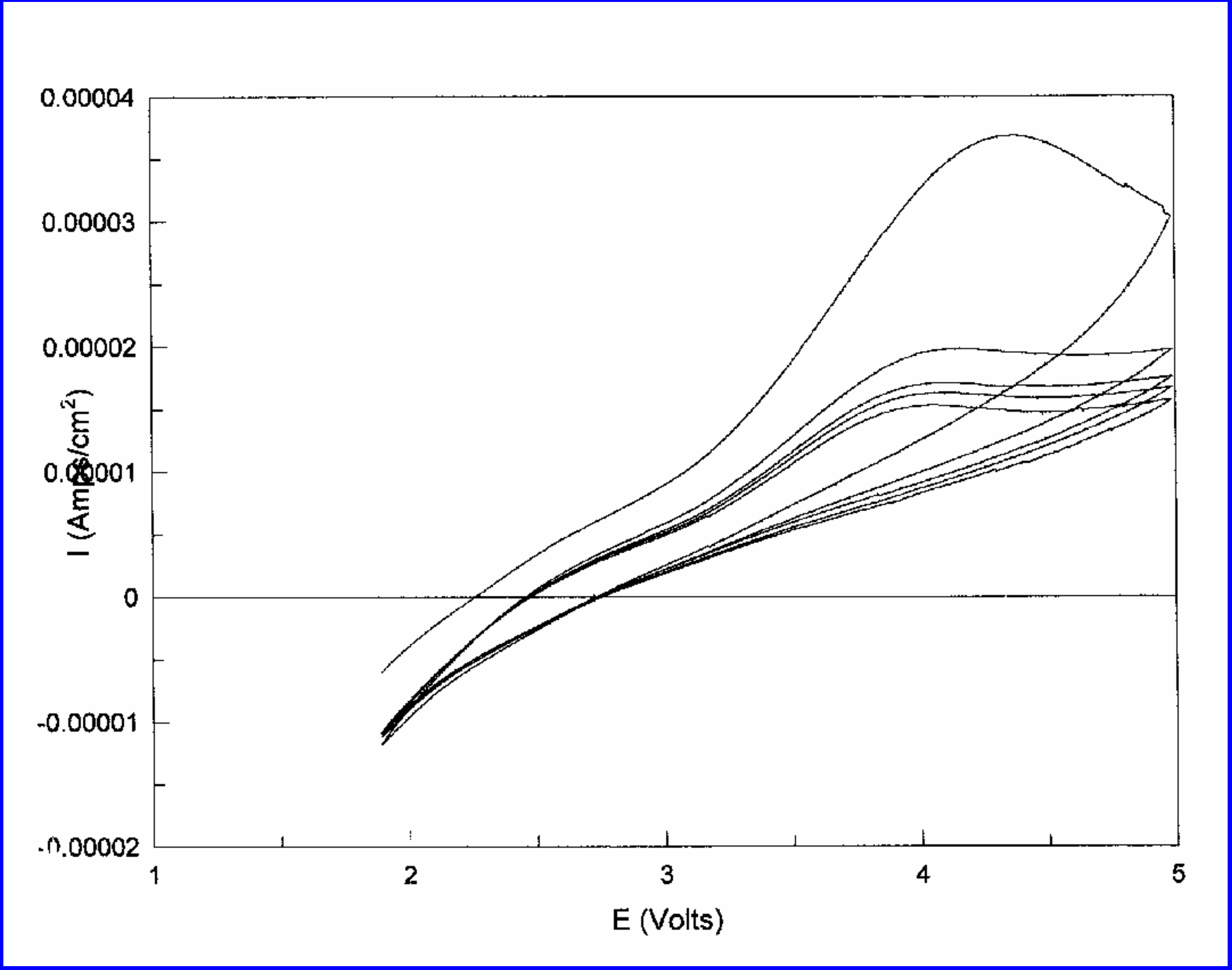


Fig. 4 Cyclic voltammograms of the $LiCoO_2$ electrode at scan rates of **a** 0.1 mV s^{-1} and **b** 0.01 mV s^{-1}, with 1 M $LiClO_4$ in PC as the electrolyte

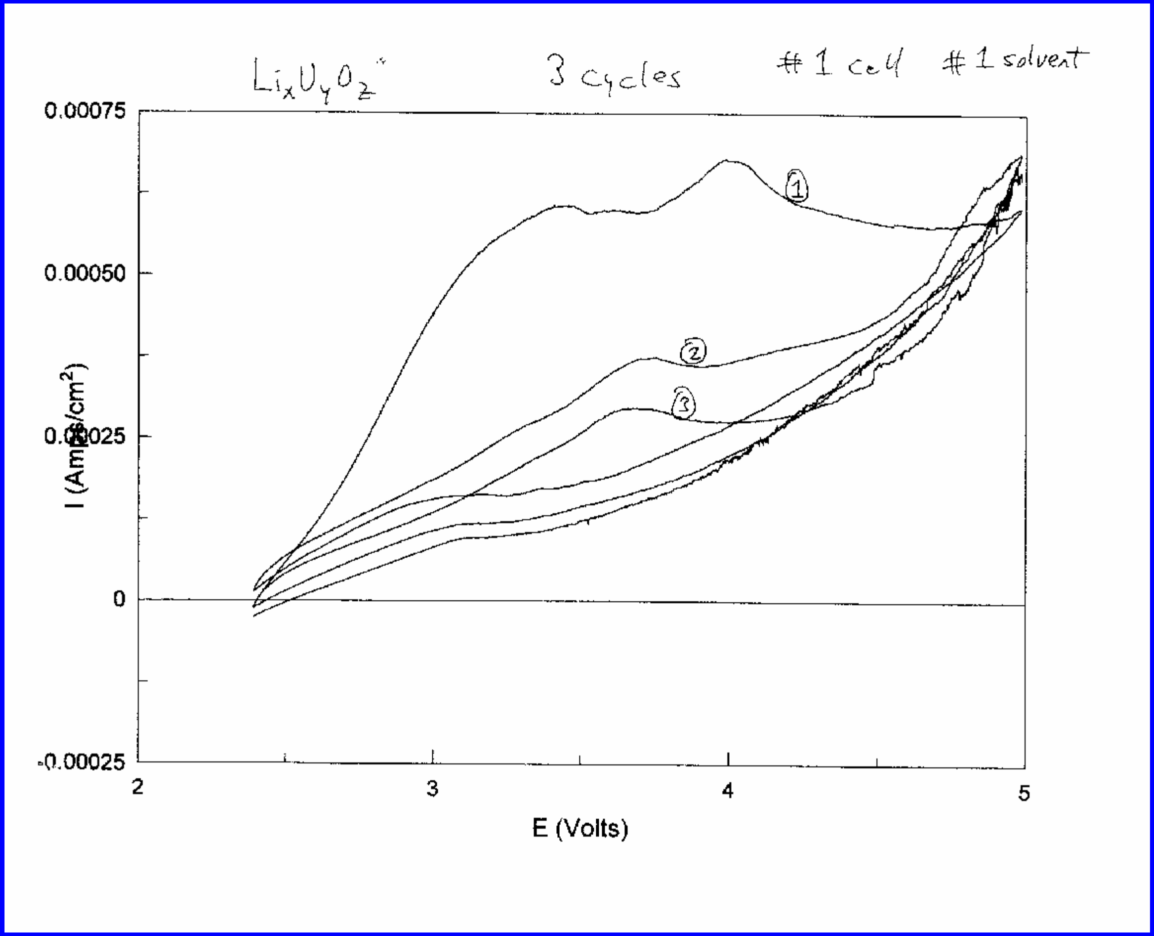
CV of UO_2 Electrode

(Lithium metal RE, Lithium metal CE
UO2 WE, 1 M Lithium Tetrafluorborate in 1:2 PC/DMC)
Fully irreversible

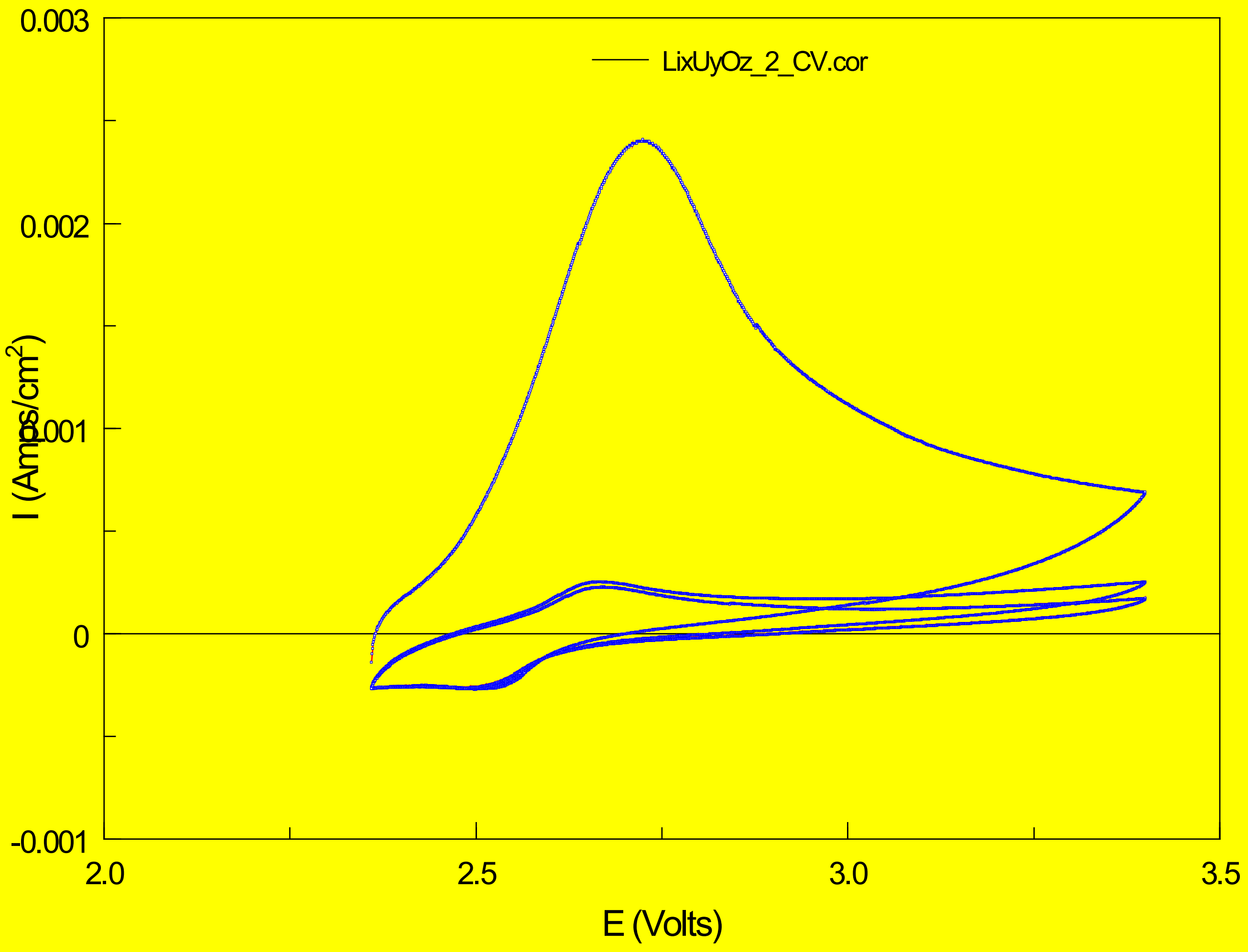


CV of our Material

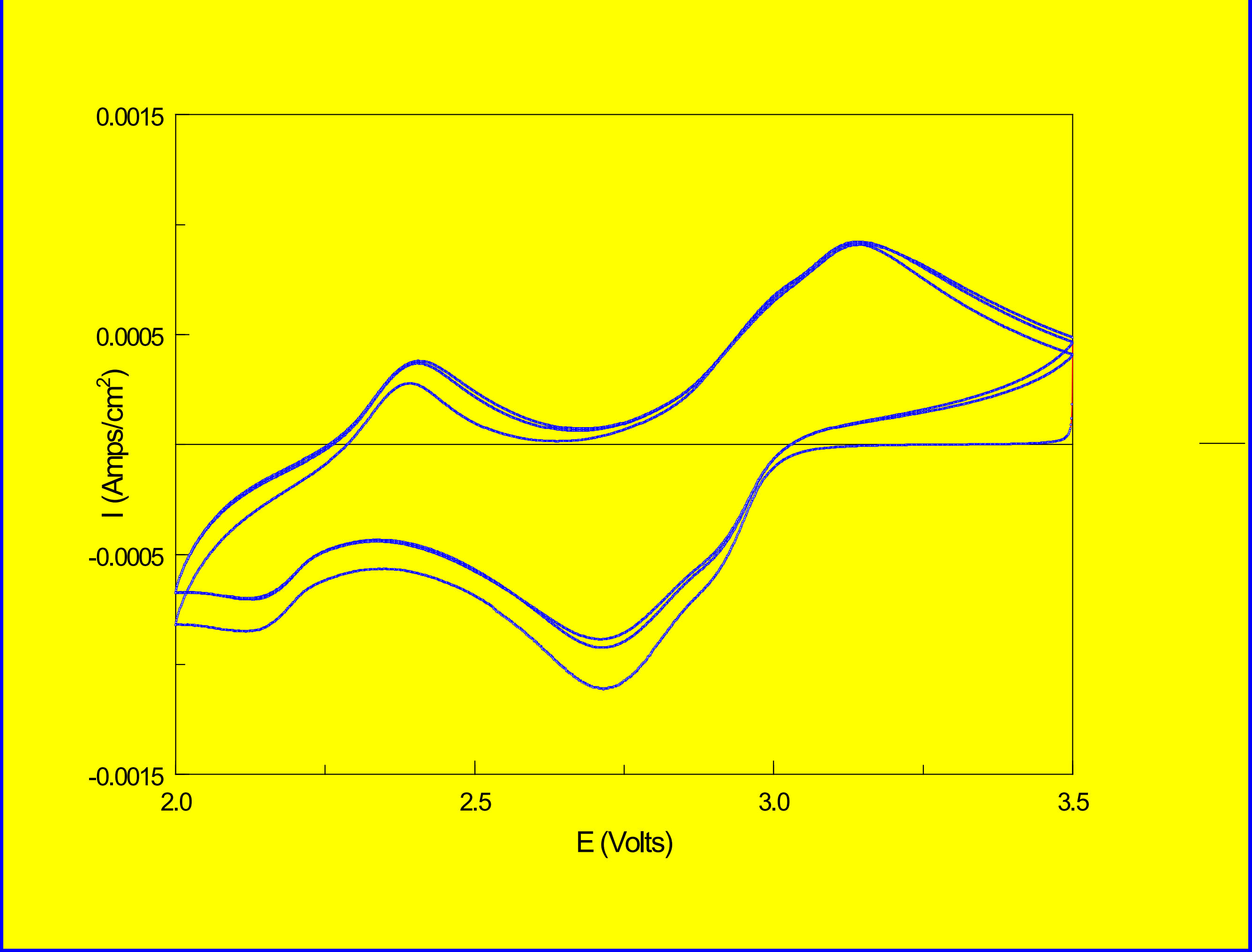
- 12 times the current as seen in UO_2 alone.
- Lithium is in the structure, but no intercalation is seen.



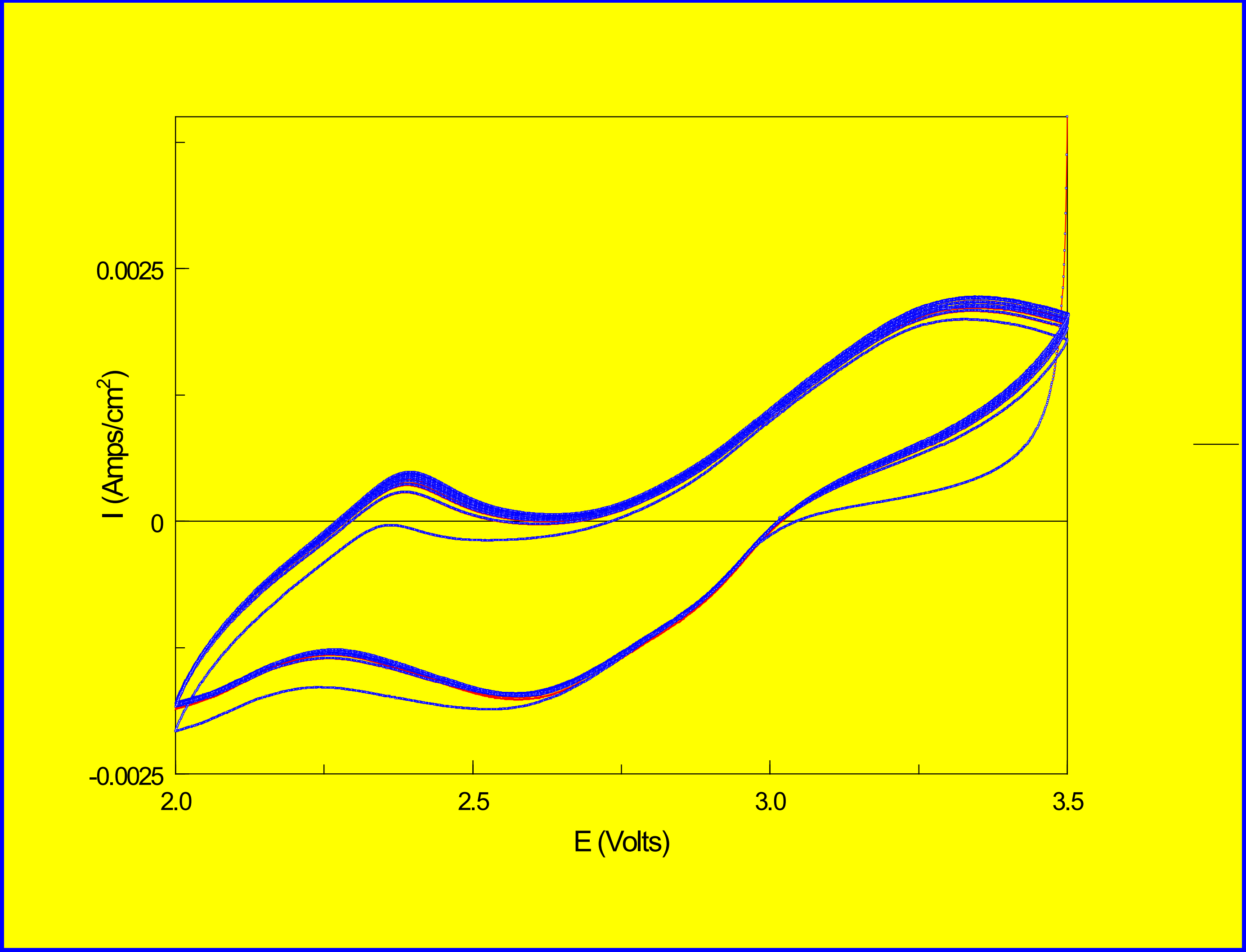
Lithium Leaves, but no re-intercalation



Fully Reversible, 3 cycles 0.1 mV/secs—Uranium X

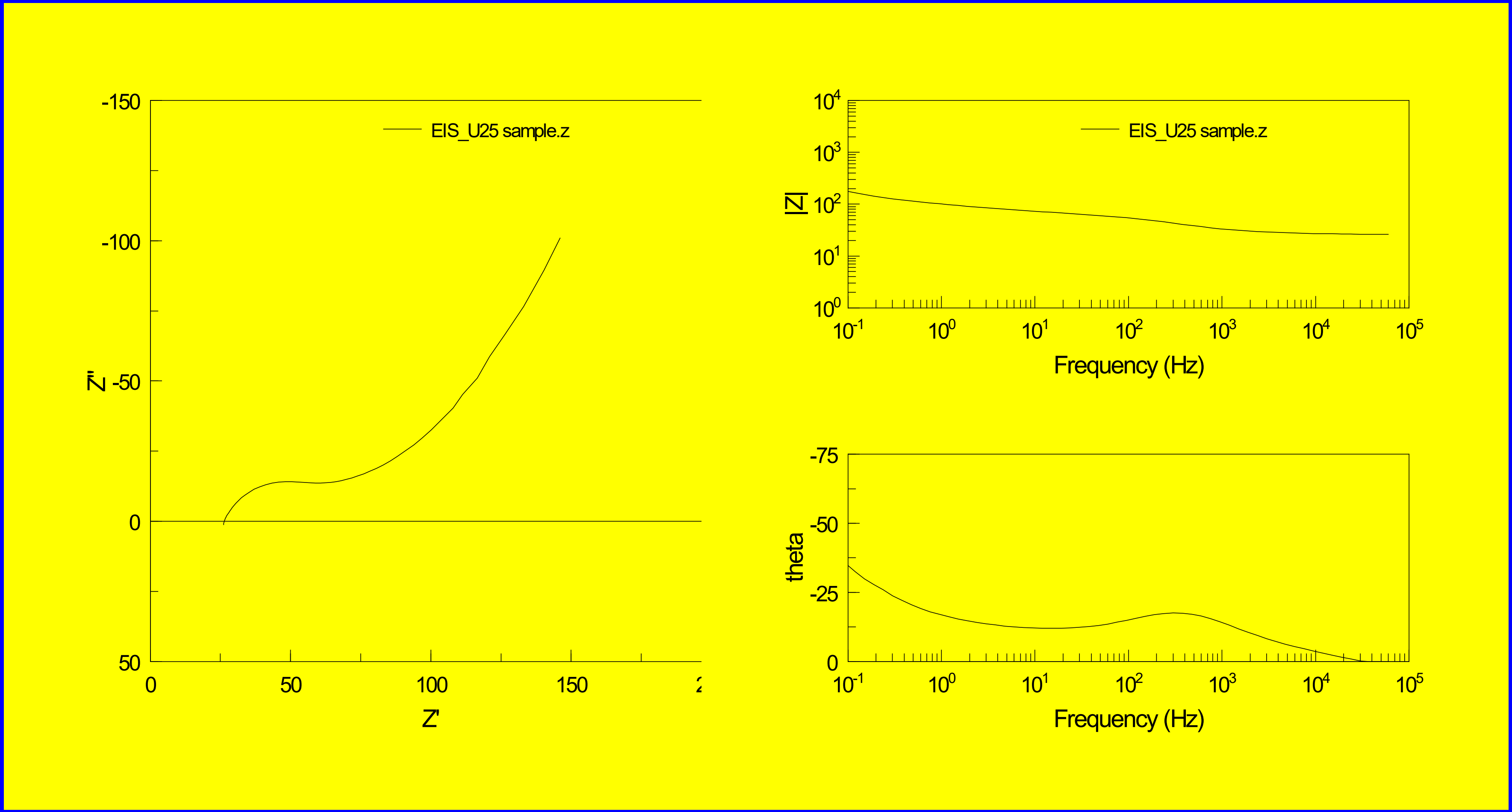


10 cycles, Very reversible 0.2 mv/secs Uranium X



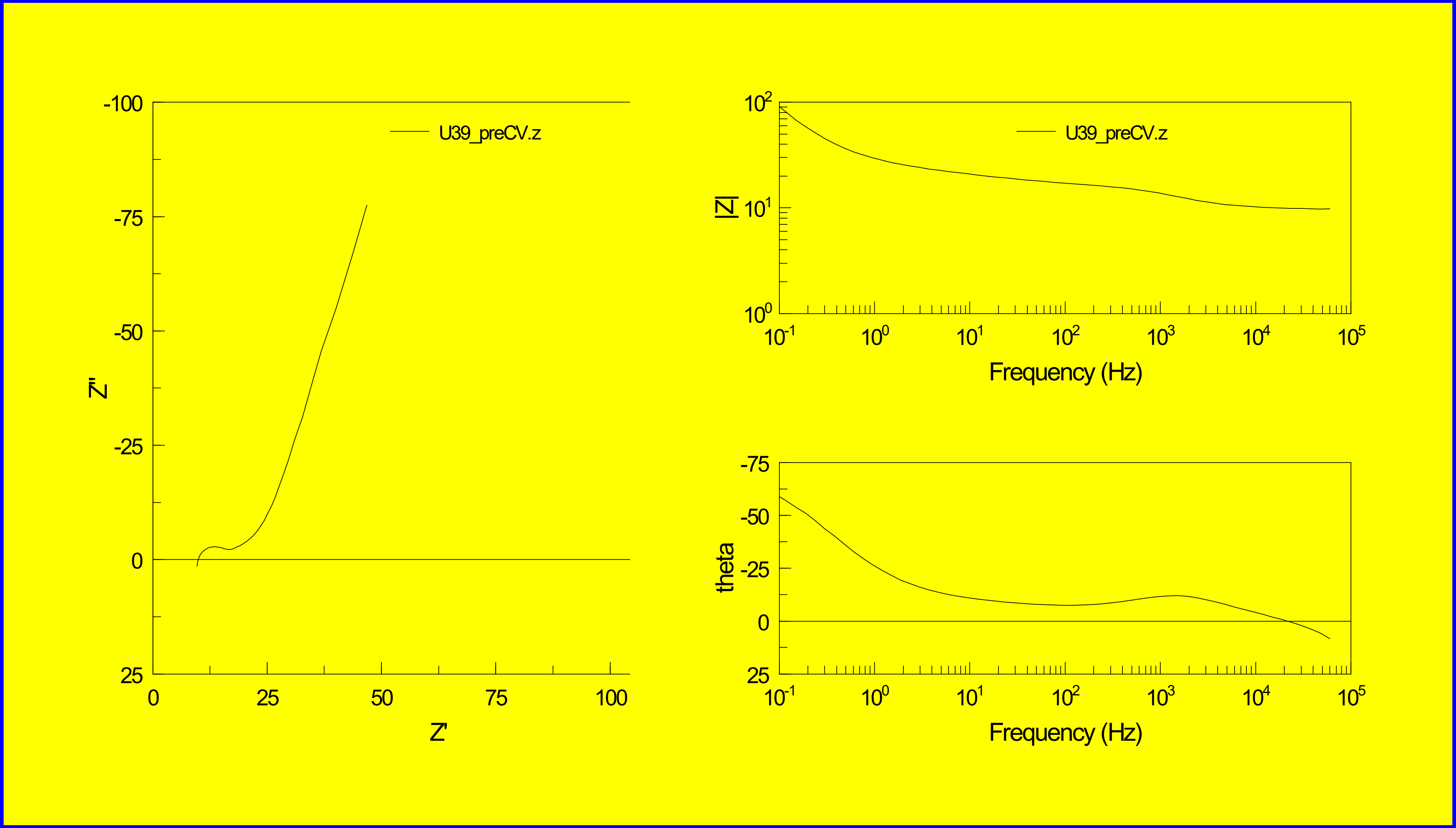
Capacitor

UO_2 EIS



EIS_U25 sample.z
-150
-100
-50
0
50
0
50
100
150
Z''
Z'
EIS_U25 sample.z
|Z|
Frequency (Hz)
theta
-75
-50
-25
0
Frequency (Hz)

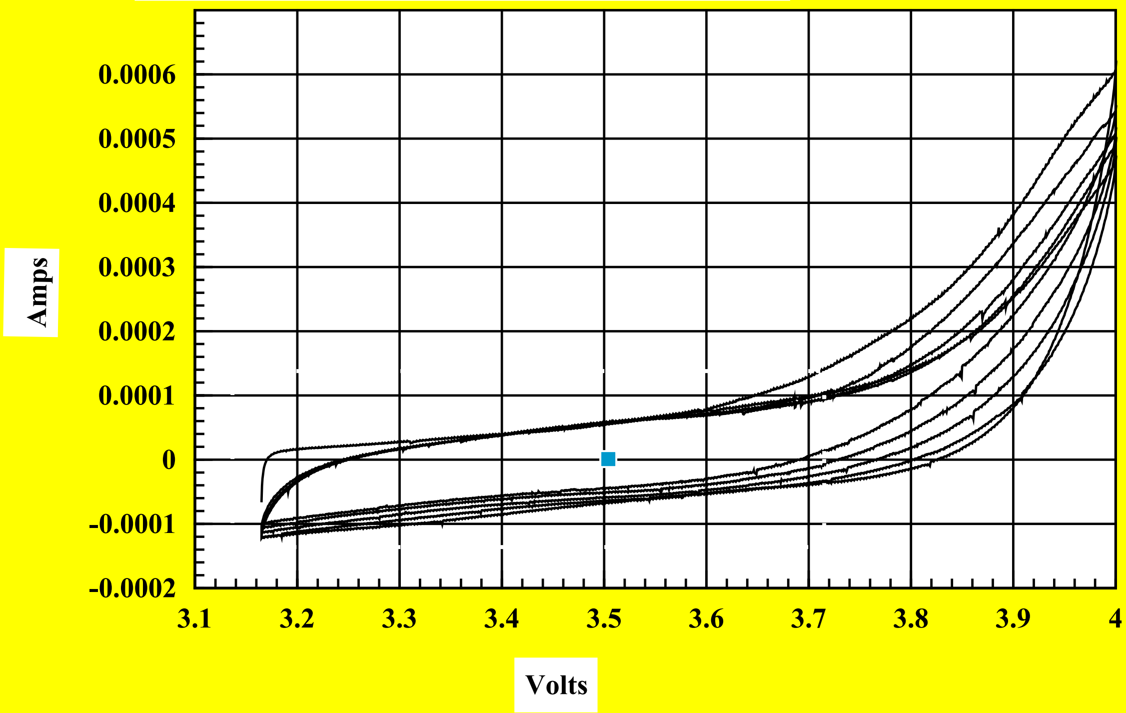
U_3O_8 EIS



U39_preCV.z
-100
-75
-50
-25
0
25
Z''
0
25
50
75
100
Z'
U39_preCV.z
|Z|
10^2
10^1
10^0
10^-1
10^0
10^1
10^2
10^3
10^4
10^5
Frequency (Hz)
theta
-75
-50
-25
0
25
10^-1
10^0
10^1
10^2
10^3
10^4
10^5
Frequency (Hz)

CV of UO2—Capacitor Material

Figure 4. Cyclic of UO2 in 1 M Tetrafluoroborate



Uranium doped Materials

Electrochemical properties of $LiMn_2O_4$ cathode material doped with an actinide

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Abstract

Metal substation as an efficient approach for improvement of battery performance of $LiMn_2O_4$ was performed by an actinide dopant. Uranium as the last natural element and most common actinide was employed for this purpose. Cyclic voltammetric studies revealed that incorporation of uranium into $LiMn_2O_4$ spinel significantly improves electrochemical performance. It also strengthens the spinel stability to exhibit better cycleability. Surprisingly, the capacity increases upon cycling of $LiU_{0.01}Mn_{1.99}O_4$ cathode. This inverse behavior is attributed to uniform distribution of dopant during insertion/extraction process. In other words, this is an electrochemical refinement of the nanostructure which is not detectable in microscale morphology, as rearrangement of dopant in nanoscale occurs and this is an unexceptional nanostructural ordering. In addition, uranium doping strengthens the Li diffusion, particularly at redox potentials.

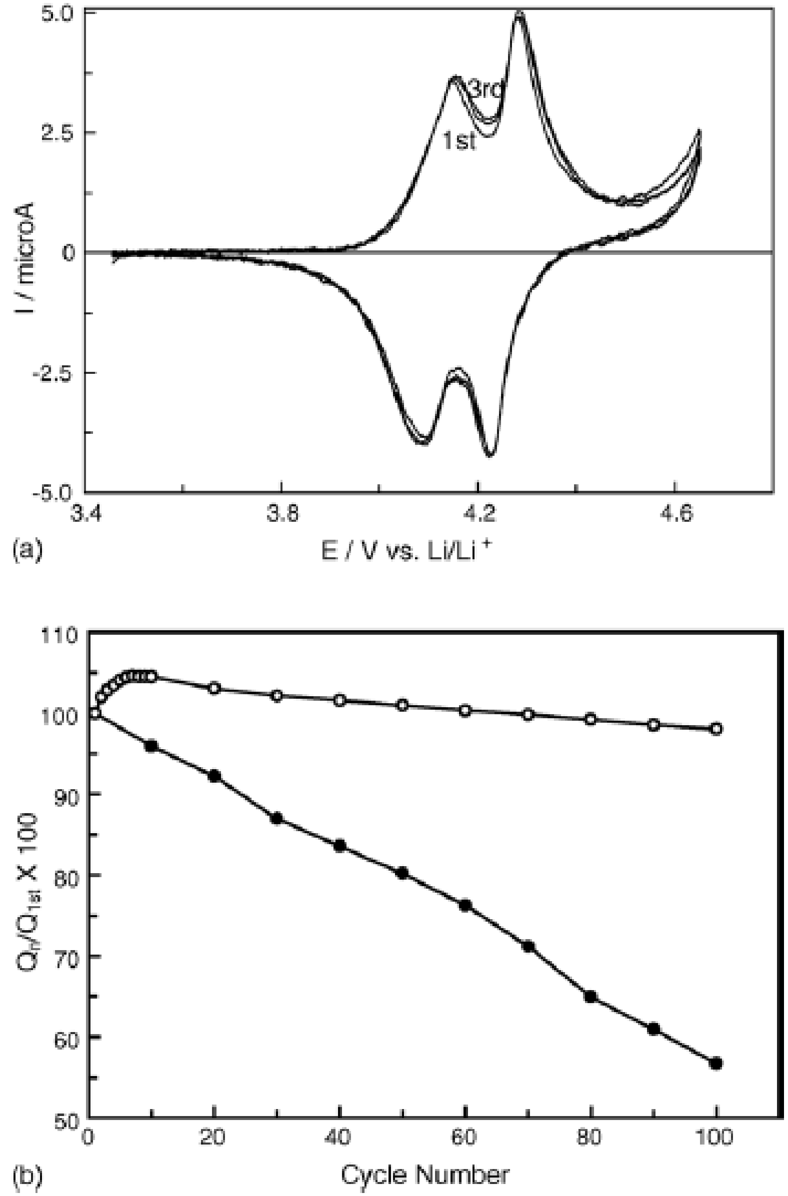

Fig. 4. Cycleability of the $LiU_{0.01}Mn_{1.99}O_4$ cathode. (a) Repetitive cyclic voltammetric behavior of the $LiU_{0.01}Mn_{1.99}O_4$ cathode in $LiNO_3$ aqueous solution with scan rate 0.1 mV/s. (b) Cycleability data for $LiMn_2O_4$ (●) and $LiU_{0.01}Mn_{1.99}O_4$ (○) cathodes as estimated from the total charge of each cyclic voltammogram.

Summary

- Newly Formulated new lithiated uranium compound $Li_xU_yO_z$ that has more than 100 times the current output of uranium dioxide by itself, but not reversible.
- Uranium X has been shown to be fully reversible with a medium current value.
- Uranium Dioxide behaves as a double layer capacitor Going to Dickens Recipe for Li_2UO_3
- Uranium doped lithiated Manganese Oxide greatly enhances cathode performance, stability, and voltage output.